DOI: 10.1002/anie.200603800

Surfactant Detection

A Simple Approach for the Selective and Sensitive Colorimetric Detection of Anionic Surfactants in Water[**]

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Since the formulation of supramolecular principles, chemists have been developing systems with enhanced functionalities.[1] More recently, the combination of chemical principles and solid structures has led to new synergic strategies, which embrace unprecedented tunability of the properties of the nanoscopic solids and new perspectives of applicability to supramolecular concepts.[2–7] We believe that one field in which these ideas might have a considerable impact is in the development of new chemical signaling protocols. For instance, the blending of models related to chemical sensors and inorganic systems has recently resulted in the preparation of hybrid organic–inorganic materials with enhanced patterns of selectivity.[8–15]

In the course of this research we have focused our attention on one type of anion of critical environmental concern,[16–18] that is, the anionic surfactants. Surfactants are water-soluble surface-active agents comprised of a hydrophobic portion (a long alkyl chain) attached to a hydrophilic (water-soluble) moiety. Anionic surfactants are of widespread importance in the detergent industry, emulsification, lubrication, catalysis, and so on, and are widely employed. As a result of their anthropogenic origin and extensive use, it is a frequent task to determine surfactants in product formulations and in industrial samples for quality and process control.[19–23] Apart from the efforts in studying methods to reduce their environmental impact, another important aspect is the development of new and improved sensing methods for their determination. Many well-known methodologies require tedious procedures (for example, liquid and gas chromatography) or the use of relatively large amounts of chlorinated solvents that are not readily biodegradable (such as chloroform in the spectroscopic "methylene blue" method),[24] in addition to the fact that these methods cannot usually be used for in situ determinations. A different approach makes use of ion-selective electrodes; however, these still show limitations in their applicability, most commonly related to reproducibility and signal stability.[25–30] As a result of these restrictions, there is a real need to develop new methods for anionic surfactant sensing in water that are applicable to a wide range of situations. In this sense, novel selective and sensitive chromo- or fluorogenic methodologies are especially appealing for the design of simple in situ screening applications.

As a part of our interest in the development of new chromofluorogenic sensing protocols for target guests,[31–36] herein we report a conceptually novel colorimetric method for the selective determination of anionic surfactants based on the use of imidazolium-containing ionic liquids on a solid support.[37–39] For this purpose, we have designed and prepared the hybrid system **S1** (see Figure 1), which was used in a two-step sensing protocol. In the first step, the contact of **S1** with a solution of anionic surfactant would result in a superficial self-assembly organization of the surfactant molecules on the cation-functionalized surface. This layer would be remarkably hydrophobic with the long alkyl chains pointing toward the bulk solution and would extract, in a second step, a suitable dye (that is, methylene blue) from water. The detection principle relies on the idea that the self-assembly process of the anionic surfactant would be selective as a consequence of unique strong hydrophobic interactions between surfactant molecules in the formed monolayer. The

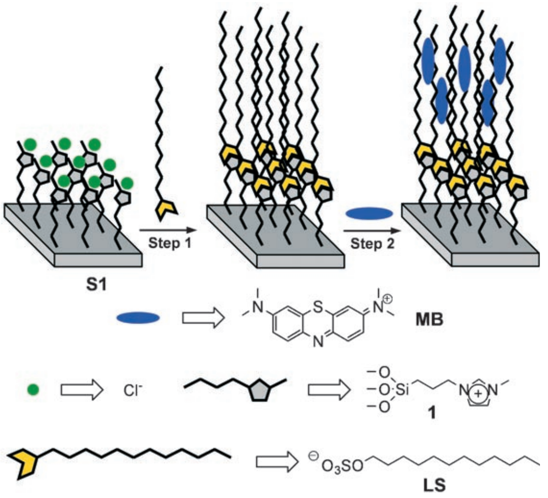

Figure 1. Representation of the two-step protocol for the colorimetric sensing of anionic surfactant using the solid **S1** grafted with imidazolium groups and methylene blue as signaling dye. MB: methylene blue; LS: lauryl sulfate.

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[**] We thank the Ministerio de Ciencia y Tecnología (projects MAT2003-08568-C03 and CTQ2006-15456-C04-01/BQU) and Generalitat Valenciana (project GV06/101) for support. C.C. thanks the Universidad Politécnica de Valencia for a doctoral fellowship. F.S. also thanks the Ministerio de Educación y Ciencia for a Ramón y Cajal contract.

final behavior signaling the presence of anionic surfactants would be bleaching of the dye solution and coloration of the solid, both visible to the naked eye.

The sensing hybrid material **S1** was readily prepared by anchoring the imidazolium derivative **1** (obtained by reaction of *N*-methylimidazole with triethoxysilylchloropropane)[40] on silica in acetonitrile at room temperature. The final solid consists of an inorganic matrix covered by imidazolium cations. Solid **S1** was characterized by using conventional solid-state techniques. The imidazolium content was determined by thermogravimetric and elemental analysis. The molar ratio between the imidazolium binding molecule and SiO_2 was 5.3×10^{-2} ($0.67\ \mathrm{mmol\,g^{-1}}$ solid), which results in a relatively dense monolayer of imidazolium cations with an average distance between neighboring imidazolium groups of approximately 10 Å. The solid **S1** contains very simple, but suitable (see below), binding sites, which opens the way to assess the use of this material in assays for colorimetric sensing of the type described in Figure 1.

The performance of **S1** as a chemosensor was studied in water. In preliminary assays, solid **S1** (50 mg) was suspended in an aqueous solution (e.g. 50 mL) containing lauryl sulfate (LS), used here as a standard anionic surfactant at a concentration of $1\times10^{-3}\ \mathrm{mol\,dm^{-3}}$. The suspension was adjusted to pH 4, stirred for about 30 min, and the solid was isolated by filtration (step 1). The hybrid solid with the adsorbed LS was then suspended in an aqueous solution of methylene blue (MB; e.g. 10 mL, $10^{-5}\ \mathrm{mol\,dm^{-3}}$) and stirred for 10 min (step 2). After this procedure the solution became colorless, whereas the solid was of a deep blue color. A similar response was also found with other common anionic surfactants, such as tetradecyl sulfate, alkylbenzene sulfonate (LAS), and partially with dodecyl phosphate (see Figure 2).

To further test the aptness of the procedure, the same two-step process was carried out for solid **S1** but with LS changed for other anions (carbonate, phosphate, sulfate, nitrate, and chloride) and cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}). In all these new cases, the solid remained white and the MB solution retained its former absorbance. Remarkably, the solid also remained white in the presence of neutral (Triton X-100) and cationic surfactants (CTAB; see Figure 2). The effect of chain length was also studied through the response of the solid to different alkyl sulfates. Thus, **S1** responds to alkyl sulfates with C_{14}, C_{12}, and partially with C_{10} linear alkyl chains, but gave no response to octyl or hexyl sulfate (not shown). A similar length-dependent response has been reported, for instance, in anionic-surfactant-selective PVC membrane electrodes.[25] These results demonstrate the suitability of the method outlined in Figure 1 through the self-assembly of the anionic surfactants on the imidazolium-covered surface and further dye adsorption.

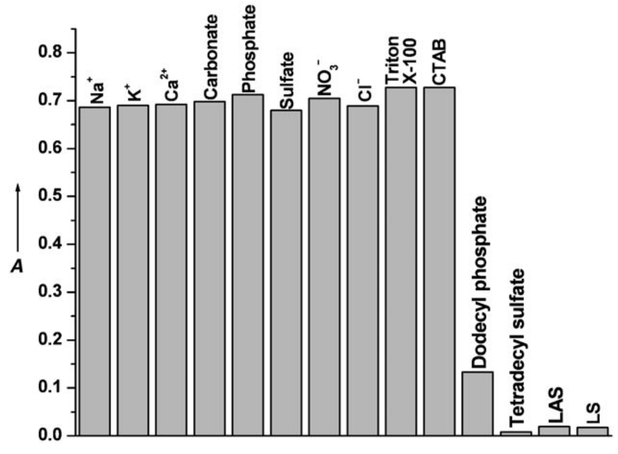

Figure 2. Methylene blue absorbance at 664 nm in the presence of certain anions and cations (see text). Solid **S1** (50 mg) with the corresponding anion or cation (50 mL, $c = 1\times10^{-3}\ \mathrm{mol\,dm^{-3}}$) at pH 4 and then MB (10 mL, $c_{MB} = 1\times10^{-5}\ \mathrm{mol\,dm^{-3}}$). CTAB: cetyltrimethylammonium bromide.

The response of the sensing material **S1** as a function of the LS concentration is illustrated in Figure 3, which plots the MB absorbance at 664 nm after the two-step protocol described above. The results reveal that the amount of dye removed from an aqueous solution by the hybrid **S1**–LS material is proportional to the extension of the formed imidazolium–LS monolayer and is relative to the amount of anionic surfactant in the former solution. By following a conventional mathematical analysis, it was found that the behavior of **S1** as a sensing material can be interpreted and analyzed by Equation (1),[41] which was deduced from the two-step paradigm shown in Figure 1; that is, 1) LS adsorption on the imidazolium surface (using Langmuir-type analysis) and 2) further extraction of the MB dye. Importantly, the shape of the curve can be tailor-made by a simple modification of the volumes of the MB and LS solutions (V_1 and V, respectively). This can be seen, for instance, in Figure 3, which shows that the increase in the total volume of the LS sample or the reduction in the volume of the MS solution is a quite simple method to reduce the detection limit or somehow

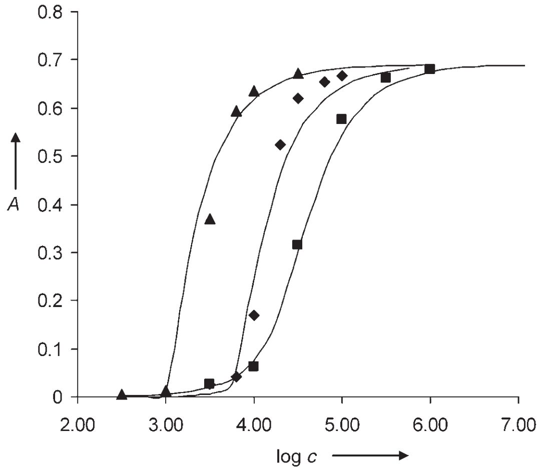

Figure 3. Methylene blue absorbance at 664 nm after the protocol shown in Figure 1 (see also text) for solutions of different concentrations of LS (from $10^{-2.5}$ to $10^{-5}\ \mathrm{mol\,dm^{-3}}$) and using an aqueous solution of MB ($1\times10^{-5}\ \mathrm{mol\,dm^{-3}}$). From left to right: curves obtained from treatment of 50 mL of LS with 10 mL of MB (▲), 250 mL of LS with 10 mL of MB (◆), and 250 mL of LS with 3 mL of MB (■). Fitting curves have been drawn by using Equation (1) (see reference [41]).

control the dynamic range of the signaling protocol. Thus, a detection limit as low as 1 ppm can be reached by using 250 and 3 mL of aqueous solutions of LS and MB, respectively.

The response of solid **S1** to LS is also observed in Figure 4, which shows a picture of **S1** solids after the two-step process using aqueous solutions containing known amounts of LS. A clear color modulation as a function of the LS concentration can be detected by the naked eye, thus supporting the suitability of the method for the development of simple, undemanding, colorimetric probes for qualitative or semi-quantitative determinations.

Figure 4. Color of solid **S1** after the two-step process shown in Figure 1 ($V = 250$ mL) using wastewater containing known amounts of LS. From left to right: $c_{LS} = 1\times10^{-3}$, 3.2×10^{-4}, 1×10^{-4}, 3.2×10^{-5}, 3.2×10^{-6}, and 3.2×10^{-7} mol dm^{-3}.

Stimulated by these favorable features of the sensing material, we took further steps to test the potential use of **S1** as a colorimetric chemosensor. As a first stage, in a control experiment, the response to LS (e.g. $c_{LS} = 3.2\times10^{-4}$ mol dm^{-3}) of the sensing material **S1** was checked in the presence of anions and cations usually found in aqueous solutions (Na^+, K^+, Ca^{2+}, Mg^{2+} phosphate, and chloride, $c = 1.0\times10^{-3}$ mol dm^{-3}; carbonate, phosphate, and nitrate, $c = 5.0\times10^{-3}$ mol dm^{-3}; sulfate, $c = 1.0\times10^{-4}$ mol dm^{-3}). In all cases, nearly the same final absorbance of the MB dye was observed, which indicates that no remarkable interference to the LS determination was found in the presence of these chemical species (see Figure 5). Eventually a certain interference in the presence of sulfate was found, but only at concentrations larger than 40–50 ppm of this anion. Yet, this would not limit the application of the probe, as the quantities of sulfate ordinarily found in natural waters are in the 10–30 ppm range.[42] In a second stage, we prospectively used solid **S1** for the determination of anionic surfactants in residual waters with good results. For example, a sample of urban wastewater (250 mL) containing 13 ppm of anionic surfactants (determined following the traditional "methylene blue" method) was filtered and found to have (12 ± 2) ppm anionic surfactants (from three measurements) by using the hybrid organic–inorganic material **S1** and a suitable calibration curve.

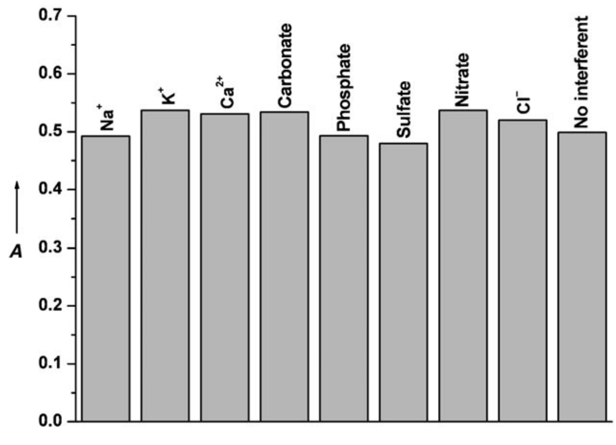

Figure 5. Methylene blue absorbance at 664 nm after the two-step protocol shown in Figure 1 for LS (3.2×10^{-4} mol dm^{-3}) in water at pH 4 and in the presence of certain anionic and cationic species.

In summary, we have developed a colorimetric protocol for the determination of anionic surfactants in water, based on supramolecular concepts through the formation of a hydrophobic nanolayer built by the self-assembly of anionic surfactants on an imidazolium-covered surface and further extraction of a suitable dye. As far as we know, this is a novel approach free of organic solvents and a suitable alternative to classical methods for rapid screening applications. Solid **S1** displays a remarkable behavior and allows the selective and sensitive colorimetric determination of this class of environmentally important anions. We believe that this procedure, based on self-assembly organization on coordinating surfaces and further dye adsorption, might be of interest as a route for the design of new and improved sensors for the rapid colorimetric screening of certain target guests of interest. Moreover, this result could encourage the search for alternatives to the extraction processes in organic phases used in classical analysis to develop new, undemanding, "green" protocols completely free from the use of hazardous organic solvents.

Received: September 15, 2006
Published online: January 22, 2007

Keywords: analytical methods · colorimetry · dyes/pigments · sensors · surfactants

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[41] $A = A_0 - \frac{\varepsilon n_{\mathrm{A}}}{V_1};\ n_{\mathrm{A}}^2 - n_{\mathrm{A}}\left[\frac{V}{K} + c_{\mathrm{LS}}\,V + n_0\right] + n_0\,V\,c_{\mathrm{LS}} = 0 \quad (1)$

where A and A_0 are the observed absorptions at 664 nm for the MB solution before and after interaction with the **S1**–surfactant system, respectively, ε is the molar absorption coefficient of the dye, and n_{A} is the adsorbed LS in the imidazolium ionic liquid monolayer (mol). Additionally, V_1 and V are the volumes (dm^{-3}) of the MB and LS solutions, respectively, n_0 is the maximum amount of adsorbed LS in the monolayer (mol), c_{LS} is the concentration of LS (mol dm^{-3}), and K is the adsorption constant.

[42] In preliminary studies, we have observed that sulfate interference is considerably reduced in the presence of Mg^{2+}.